

**METHOD FOR REMOVING CONTAMINANTS
FROM THERMALLY CRACKED WASTE OILS**

BACKGROUND OF THE INVENTION

5 1. Field of the Invention

The present invention relates to the removal of contaminants from thermally cracked waste oils, and more particularly, to the application of an accelerated solvent extraction process for removing contaminants from thermally cracked waste oils such as 10 waste engine oil, metal cutting oil and hydraulic oils.

2. Related Art

A variety of processes have been developed for the production of diesel fuel from waste oils such as used engine oils and hydraulic 15 oils by thermal cracking process. However, regardless of the processes of the technologies developed so far, the thermal cracking process itself gives rise to unavoidable problems of the quality of the end product oil. The end product oil has a strong odor mostly generated from sulfur compounds, dark tar precipitates 20 originated from oxidation and the oil becomes darkened as it ages. These problems give rise to questions on the process itself and marketability of the end product oil.

U.S. Patent No. 5,855,768 issued in Jan 1995 to Stanciulescu et al. discloses that 95% of tar is removed by methanol extraction 25 method at the same time with removal rate of 60% sulfur, 90% nitrogen

and 60% chlorine. The temperature employed was between room temperature and 60°C which is below the boiling point of methanol. It is well described by Stanciulescu et al. that the thermal cracking process produces olefin-rich oil which rapidly changes color and 5 composition due to oxidation and polymerization reactions. This is also pointed out in "A literature review on fuel stability studies with particular emphasis on diesel fuel", Energy & Fuels, vol. 5, 2, 1991 written by Balts, B.D. and Fathoni, A.Z. This paper gives full explanation on the tendency of deterioration of thermally 10 cracked distillates more rapidly than straight run distillates during storage and that cracked product oils induce gum and sediment formation in fuels. It was claimed from the review that major causes of gum or sediment formation include oxidation, auto-oxidation and chemical reactions such as polymerization involving 15 unsaturated hydrocarbons and/or reactive organic compounds of sulfur, nitrogen and oxygen present in the fuel.

The article "Influence of methanol extraction on the stability of middle distillate fuels" in Fuel, 73(2), 269-271 (1994) written by Sharma, Y.K. and Agrawal, K.M. also describes 20 about methanol extraction. Its research data proves that middle distillate extracted with methanol shows much less insolubles, which proves the effective removal of insoluble precursors.

U.S Patent No. 5,446,231 issued to Arganbright et al. on Aug 29, 1995 also shows a method for the removal of nitrile 25 contaminants from C5 streams in which methanol may be used as an

extraction solvent. U.S. Patent No. 4,746,420 issued to Daren et al. on May 24, 1988, have also found that methanol may be used as co-solvent in the removal of nitrogen compounds from diesel oils.

5. Wecher, M.A. and Hardy, D.R. investigated methanol extraction in "The isolation of precursors responsible for insolubles formation in mid-distillate diesel fuels" in Fuel Science and Technology International, 7(4), 423-441 (1989). This paper claims that when mid-distillate diesel fuel is subject to 10 solvent extraction using methanol, insolubles in the fuel are reduced dramatically, with more than 95% of the fuel insolubles being soluble in methanol.

Accelerated Solvent Extraction (ASE) method has been developed and taken as an analytical method by U.S. Environmental 15 Protection Agency (EPA) where elevated temperature and pressure are applied. However, the solvent extraction process has not been applied at elevated temperature and pressure to the removal of contaminants from thermally cracked waste oils and the optimum range of the high temperature and pressure has not been investigated. 20 Perfect or full contact of methanol with contaminants in the cracked oil is not made by conventional batch type extraction processes running at room temperature and atmospheric pressure where mixing is totally dependant on mixing blade.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the invention to provide a method for removing contaminants from thermally cracked waste oils such as engine oil with respect to obtaining better 5 productivity using high temperature and pressure than any other processes developed by now.

It has been found from the present invention that the contaminants containing sulfur and nitrogen from the thermally cracked distillates may readily be removed at much faster rate 10 at high temperature and pressure in solvent extraction than by conventional batch type extraction process which runs at room temperature and atmospheric pressure. In the invention, the substantial amount of contaminants containing sulfur and nitrogen 15 is separated into the solvent and the contaminants can be separated from the solvent by simple flash evaporation and then the solvent can be recycled.

As confirmed in the prior art of U.S. Patent No. 5,855,768, the solvent extraction with methanol must be carried out within short period of time after thermal cracking process, preferably 20 within 24 hrs. However, it is confirmed from the present invention that leaving the thermally cracked oils more than 6 hrs at room temperature makes the solvent extraction process more difficult or ineffective at all. By employment of methanol extraction within short period of time, preferably within 0 ~ 20 min, substantial 25 amount of contaminants could be removed after a series of repetitive

methanol extractions.

Preferably, the first extraction is carried out for a mixture of methanol and the thermally cracked oil at a ratio of 50:50 by volume and the second extraction is carried out for a mixture of 5 methanol and oil (treated by the first extraction) at a volume ratio of 40:60. Then, the oil treated by the second extraction is mixed with 20% (by vol.) methanol for the storage of the final end product oil. The first and second extractions are carried out for 3 ~ 15 min at 50 ~ 70° C and 30 ~ 55 psi for the completion 10 of the entire extraction process.

The extraction process between methanol and the oils is carried out in a pressure vessel equipped with a thermal electric jacket and a mixer. Pumping methanol by a high-pressure pump mainly generates pressure.

15 The result of using methanol extraction process at high temperature and pressure shows much faster reaction rate and produces better quality of end product oil. Each methanol solvent extraction takes 3 ~ 5 min before completion of the reaction compared to 40 ~ 70 min of conventional continuous batch type extraction 20 process at room temperature and atmospheric pressure. The sulfur contents drops to 69% and the nitrogen contents to 96%. And the tar contents decreases by 97 ~ 98%, which is 2 ~ 3 times faster rate than that of batch type extraction process. When continuous process is employed then the difference of reaction time and quality 25 of end product oil would be greater.

BRIEF DESCRIPTION OF THE DRAWINGS

The above object and other advantages of the present invention will become more apparent by describing in detail preferred embodiments thereof with reference to the attached 5 drawing in which:

FIG. 1 shows a flow diagram of the contaminant removal process which employs methanol extraction according to the embodiment of the present invention.

10 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Preferred embodiments will be described with reference to the accompanying drawing. Referring to FIG. 1, waste oils such as engine oil, metal cutting oil and hydraulic oils are thermally cracked in a thermal cracking unit. The thermally cracked oil is 15 collected using a distillation tower and a condenser, and then is transferred into a first pressure vessel 5. Recycled 99.8% methanol is also pumped into the first pressure vessel 5 using a high-pressure pump 41 to increase the pressure within vessel 5. The temperature of the thermally cracked oil at the end of the 20 condenser is about 30° C. The temperature of vessel 5 increases using an electrical thermal jacket 48 and is kept constant at a temperature of 50 to 70° C. The temperature of vessel 5 usually drops as the recycled methanol is pumped into vessel 5 by high-pressure pump 41. Therefore, vessel 5 usually keeps its

temperature higher than desired to prevent excessive temperature drop. Another option could be using a preheating heating coil wound around a methanol supply line when methanol is pumped into vessel 5. Within vessel 5, the first extraction process is performed.

5 The desirable pressure within vessel 5 is 30 ~ 55 psi and the volume ratio of methanol and cracked oil is 50:50. To keep the amount of methanol within vessel 5 constant, fresh methanol is supplied to vessel 5 from a fresh makeup MeOH.

After the first extraction process, the resulting mixture 10 is transferred to a first decanter 6 using a pump 24. Then, the methanol phase containing contaminants floats to the top of decanter 6 and is pumped to a solvent flash tank 11 by a pump 51. In solvent flash tank 11, contaminants are separated from methanol 15 liquid phase by simple flash evaporation and then discharged as a sludge cake. The operating temperature range of methanol solvent flash tank 11 is 70 ~ 80° C and the condenser 42 operates at below 45° C. The methanol treated in solvent flash tank 11 is transferred through a condenser 42 to a methanol storage tank 12 for recycling.

For the second extraction process, the primarily cleaned 20 oil is pumped to a second pressure vessel 7 using a pump 25. The recycled methanol is transferred to vessel 7 using a high-pressure pump 31 in the same manner as with the first vessel 5. The temperature within vessel 7 is also kept constant at a temperature of 50 to 70°C as described above. The desirable pressure is 30 ~ 55 psi

and the volume ratio of methanol and cracked oil is 40:60.

After the second extraction process, the resulting mixture is transferred to a second decanter 8 using a pump 26. Then, the methanol phase containing contaminants floats to the top of 5 decanter 8 and is pumped to solvent flash tank 11 by a pump 53.

The secondarily cleaned oil is sent through a pump 27 into a storage tank 10 and mixed with recycled methanol at the volume ratio of 80:20. The resulting mixture within storage tank 10 is stirred with a mixer at slow speed. Some of the methanol floating 10 to the top of storage tank 10 is sent to a vessel 9 and then transferred to solvent flash tank 11 by a pump 52. The mixture is subjected to batch type phase separation or centrifugal separation before shipping the end product oil.

In the method of the present invention, condensers 45, 46 15 and 47 are used to prevent any evaporation of methanol into atmosphere resulting in loss of the methanol solvent and possible coagulation of tar materials. The pressure gauges 43 and 44 can be equipped with pressure valve to control over pressure and to collect pressure information.

20 Table 1 shows typical chemical analysis of an example of the waste oil and product oil to which the method of the present invention is applied.

Table 1

	Waste Oil	Product Oil
Water (%)	6.00	0.05
Ash (%)	2.47	<0.01
Sulfur (%)	0.213	0.069
Carbon (%)	83.02	82.65

Hydrogen (%)	14.26	13.23
Nitrogen (ppm)	489	98.5
Specific Gravity, 24/25° C	0.905	0.807
Specific gravity, 15/15° C	0.909	0.819
Ignition point (°C)	42	38
Density-API	24.23	40.39
Heating Value (BTU/lb)	18963	19631
Color-ASTM	NA	2.5

Hereinafter, the resulting example of each process step will be described.

5 [Example of the first extraction step]

A mixture of 500ml cracked oil and 500ml methanol was used as a sample. The sample from vessel 5 has been taken at given time intervals and the results are shown in Table 2.

Table 2

	0 min	1 min	2 min	3 min	4 min	7 min
Sulfur(%)	0.213	0.187	0.101	0.085	0.086	0.085
Nitrogen(ppm)	489	193.9	78.5	47.8	46.3	46.5
Oil yield(%)	100	96.6	94.3	93.4	93.3	93.5
Residue yield(%)	0	3.4	5.7	6.6	6.7	6.5
Color(ASTM)	7.5	6.0	4.0	3.5	3.5	3.5

10 *specific gravity of sulfur --- 0.87

**specific gravity of methanol --- 0.79

The resulting oil obtained at 3 min is not very stable even though sulfur and nitrogen contents substantially decreased since 15 small amounts of tar forms as it ages. The sample obtained from vessel 5 at 3 min has been used for the second extraction process.

[Example of the second extraction step]

A mixture of 600ml cracked oil and 400ml methanol was used as a sample. The sample from vessel 7 has been taken at given time 20 intervals and the results are shown in Table 3.

Table 3

	0 min	1 min	2 min	3 min	4 min	7 min
Sulfur(%)	0.085	0.074	0.070	0.069	0.070	0.068
Nitrogen(ppm)	47.8	35.3	23.2	19.7	19.8	19.7
Oil yield(%)	100*	99	98.5	98.5	98.5	98.5
Residue yield(%)	0	1	1.5	1.5	1.5	1.5
Color(ASTM)	3.5	3.5	3.0	2.5	2.5	2.5

* The value is corrected back to 100 for comparison.

The resulting oil obtained after the second extraction step
5 remains very stable with respect to tar formation, color change
and smell. Mixing the final product oil with 20% (vol.) methanol
in storage tank 10 completes the entire extraction process and
produces stable oil with much less odor. Methanol extraction at
high temperature and pressure is proven to be very quick process,
10 which completes whole extraction process within 10 ~ 15 min.

Table 4

Sulfur reduction	Nitrogen reduction
68%	96%

As described in Table 4 the reductions of sulfur and nitrogen
are 68% and 96%, respectively, after the second extraction process.
15 Final conditioning extraction process in storage tank 10 for the
mixture of secondarily cleaned oil and methanol at the volume ratio
of 80:20 lowers further oxidation problem and increase the sulfur
and nitrogen reduction rate up to 1.0%.

Although the preferred embodiment of the present invention
20 has been disclosed for illustrative purposes, those skilled in
the art will appreciate that various modifications, additions and
substitutions can be made without departing from the scope and
spirit of the invention as defined in the accompanying claims.